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Molecular Orientation of the Silver Tetraneopentoxyphthalocyanine and Stearic Acid Mixed Langmuir-Blodgett Film and Its Chemical and Electrochemical Behaviour

By

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Molecular Orientation of the Silver Tetraneopentoxyphthalocyanine and Stearic Acid Mixed Langmuir-Blodgett Film and Its Chemical and Electrochemical Behavior

by Yansong Fu and A.B.P. Lever*

Abstract

Mixed Langmuir-blodgett films comprised of various relative concentrations of silver tetraneopentoxyphthalocyanine (AgTNPc) and stearic acid are reported. Electronic spectroscopic polarisation data are discussed in terms of the relative orientation of aggregated AgTNPc domains in the film. Electrochemical data confirm the oxidation of $Ag^{II}TNPc(-2)$ successively to $[Ag^{III}TNPc(-2)]^+$ and $[Ag^{III}TNPc(-1)]^{2+}$ in the film phase without loss of orientation. The film was also subject to chemical oxidation and reduction and the degree of organisation following such chemistry is discussed. $Ag^{II}TNPc(-2)$ aggregates, even when diluted with stearic acid, do not display resolved ESR spectra but ternary film mixtures of $Ag^{II}TNPc(-2)/H_2TNPc(-2)$/stearic acid do exhibit such resolved spectra.

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Introduction

The phthalocyanines,[1,2] known for some 60 years, and used primarily in the dye, paint and ink industry, now seem ready for exploitation in a wide range of other diverse applications.[3] The Langmuir-Blodgett (LB) technique for generating monolayer structures has considerable promise for commercial applications involving these phthalocyanine species.[4] Such applications include electrochromic devices,[5] molecular electronics[6,7], switching devices[8] and, especially, chemical gas sensors.[9-12] Success is largely dependent on the degree of the molecular organization within the film and the ability to control and reproduce such organization. Recently, Vandevyver and Barraud[13] have reviewed the techniques for the LB film characterization, among which linear dichroism measurement,[14,15] grazing incidence reflection infrared spectroscopy[16] and ESR spectroscopy[17,18] are the most convenient and commonly available methods to investigate molecular orientation in the film.

We have recently described[19] the preparation and characterization of a new soluble silver^{II} phthalocyanine, Ag^{II}TNPc (TNPc = tetraneopentoxyphthalocyanine). The solubility in a range of non-donor organic solvents provides a means of studying silver phthalocyanine in a fashion unavailable previously for the insoluble unsubstituted analogue. The neopentoxy groups are randomly distributed among the 3 and 4 positions of the outer benzene rings so that this species is isolated as a mixture of geometric isomers which are not separable by the usual chromatographic procedures. Nevertheless it has proven possible to generate organized films therewith.

The present study describes the formation of a mixed LB film of Ag^{II}TNPc and stearic acid which is characterized using dichroism measurements to show the average molecular orientation of the film. Strong intermolecular aggregation is present as monitored by UV-Vis and ESR spectra.

While it is sometimes difficult to transfer a pure phthalocyanine monolayer onto a solid substrate, a mixture of the phthalocyanine with some long chain amphiphilic species, such as octadecanol,[20] stearic[21-23] or arichidic acid,[24] has proven effective. It would be interesting to know how the long chain species such as stearic acid functions in the film, and how this might affect the molecular orientation and the chemistry of the co-partner. The understanding of this issue is important to the utility of those long chain hydrocarbon species in making mixed LB films.

To further characterize the film, linear cyclic voltammetry (LCV) and differential pulse cyclic voltammetry (DPV) were carried out on the film deposited on a SnO_2 film-coated glass slide. The stability of the molecular organization within the film was also investigated by monitoring the change in dichroic ratio of the film upon electrochemical or chemical modification.

Experimental Details

Materials: Metal-free tetraneopentoxyl phthalocyanine (H_2TNPc) was prepared following the literature methods.[25] Silver^{II} tetraneopentoxyphthalocyanine (Ag^{II}TNPc) was prepared according to the recently described method.[19] Toluene, as spreading solvent, was Aldrich HPLC grade and glass distilled. The subphase was water purified by double distillation over $KMnO_4$ followed by passage through a Barnstead organic removal cartridge and two Barnstead mixed resin ultrapure cartridges.

Spectroscopic and Electrochemical Methods: The film electronic spectra and dichroic ratio were measured with a Hitachi Perkin - Elmer Microprocessor 340 spectrometer. Polaroid film polarizers were mostly employed, but some late experiments used calcite polarizers and a Cary 2415 spectrometer. A Varian E4 EPR spectrometer was used to record ESR spectra. Cyclic and differential pulse voltammetry were performed with a Princeton Applied Research (PARC) model 173 Potentiostat/Galvanostat, controlled by a PARC 175 Universal Programmer, and a PARC 174A Polarographic Analyzer. Spectro-electrochemical data were collected with a Guided Wave Inc. model 100 Spectrum Analyzer and the PARC model 173 Potentiostat.

Preparation of the LB Film: The LB trough was built at York following a described design.[26] The measurements of surface pressure (π) versus area per molecule (A) isotherms and multilayer deposition were carried out with an Apple II+ microcomputer controlled LB system, using a local program. In general, a monolayer was compressed at a speed of 1.5 $Å^2$/molecule/min. and then transferred onto a substrate at 5 mm/min. Before the actual deposition, about 10 minutes are allowed for the self-organization of the molecules after forming the monolayer. Surface pressure was measured based on Wilhelmy's principle,[27] calibrated with a stearic acid monolayer, whose collapse pressure was reported to be 40 mN/M.[27] The spreading solution was usually of 8×10^{-4} M and the deposition pressure was about 20 mN/M.

Glass and quartz slides were first treated with boiling CH_2Cl_2 or $CHCl_3$ and then sonicated in a 1 M NaOH aqueous solution. The resulting hydrophilic surface of the slide was made hydrophobic by immersing the slide in a 5% (Vol.) Me_2Cl_2Si/CCl_4 (Me - methyl) solution for a few minutes. For SnO_2 film-coated glass slides, a slightly basic Decon solution was used instead of the NaOH solution. A carefully stored, cleaned slide is usable for a few days before re-cleaning would be necessary.

Results and Discussions

Pure Ag^{II}TNPc Monolayer: Figure 1 (curve a) shows the surface pressure (π) versus area per molecule isotherm for a pure Ag^{II}TNPc monolayer. The monolayer has a fairly large compressibility, as implied by the fact that the surface pressure begins to rise at about 90 $Å^2$ and collapses at about 55 $Å^2$, giving an area of 35 $Å^2$ for the compression. The large compressibility is attributed to the interaction between the neopentoxyl groups of the molecule. It can also be seen that the monolayer collapses at a relatively low pressure, around 16 mN/M, suggesting that a fragile monolayer has been formed on the subphase. The fragility of the film led to a poor deposition ratio (the area loss on the subphase surface over the area coated on the solid substrate), being only 0.2 or so, and thus, no useful film of pure Ag^{II}TNPc was obtained. The low collapse pressure of the Ag^{II}TNPc monolayer is due to the large compressibility causing the monolayer to fold easily. In addition, the area per molecule of the monolayer at zero surface pressure was found to be 76 $Å^2$, indicating a tilted orientation of the phthalocyanine macrocyclic plane with respect to the subphase surface.

Mixed Films of Ag^{II}TNPc and Stearic Acid: When a single-component monolayer shows a poor deposition property, improved behaviour can often be observed by mixing the pure monolayer with some long chain hydrocarbon alcohol or acid. In our study, stearic acid ($C_{18}H_{36}O_2$, SteA) was mixed with the Ag^{II}TNPc species to improve the deposition ratio. The pressure isotherm of the Ag^{II}TNPc(-2)/SteA mixed monolayer with a molar ratio of 1:2 = Ag^{II}TNPc:SteA is also shown in Figure 1 (curve d). Compared to curve (a) in the same figure, the mixed monolayer showed a much smaller compressibility and a higher collapse pressure (26 mN/M), indicating that a more compact monolayer had been obtained.

The mixed monolayer can be readily deposited onto hydrophobic surfaces of different kinds of solid substrates, such as a glass/quartz slide, SnO_2 film-coated glass slide, and an HOPG (highly-oriented pyrolytic graphite) plate, all with a deposition ratio of nearly unity. The total molecular area occupied by the mixed monolayer on the water surface equals the sum of the individual molecular areas of the two components within experimental error when assuming the molecular areas to be 76 $Å^2$ for Ag^{II}TNPc and 21 $Å^2$ for SteA. This observation suggests that the Ag^{II}TNPc molecules and SteA molecules all have direct contact with subphase surface, indicative of immiscibility of the Ag^{II}TNPc and stearic acid components.

The Ag^{II}TNPc molecules are believed to be packed tightly by the SteA molecules; when a hydrophobic substrate is dipped into the water, its surface interacts with the

SteA hydrocarbon long chain strongly enough to bring the entire mixed monolayer onto the substrate. X-type transference (the monolayer can only be transferred upon the downward stroke of a substrate) was observed, which probably suggests that after the first layer was transferred, the deposition of the successive layers involved only the interaction between the neopentoxyl groups of the Ag^{II}TNPc and the hydrocarbon long chains of the SteA.

In Figure 2, the electronic spectrum (curve a) of the mixed film displays a normal Soret band at 350 nm and a Q-band at about 620 nm with a shoulder at about 680 nm. The 620 nm Q-band is blue shifted from the corresponding band in solution,[19] indicative of strong inter-molecular aggregation;[23,28,29] the 680 nm shoulder probably indicates a small amount of monomer species exists in the film, though it could arise from transitions within low symmetry aggregated species.[29]

One of the Ag^{II}TNPc(-2)/SteA mixed films was washed off the glass slide with toluene and the spectrum of the resultant solution (about 10^{-5}M) was taken, as shown in Figure 2-b. The spectrum looks identical to that of a newly-prepared Ag^{II}TNPc(-2)/toluene solution,[19] suggesting that no chemical change has occurred to the Ag^{II}TNPc molecules.

The inset in Figure 3, an ESR spectrum taken from an Ag^{II}TNPc(-2)/SteA (molar ratio, 1:2) mixed film, shows only a single broad peak arising from the unpaired electron in the Ag^{II} ion. The strong inter-molecular interaction has obscured the hyperfine coupling due to the silver nucleus and the four nitrogen nuclei, which otherwise should yield eleven peaks.[19,30]

However, using a ternary film composed of Ag^{II}TNPc(-2)/H_2TNPc(-2)/ SteA (1:11:24), hyperfine coupling was observed with anisotropic g values (Figure 3). Thus in this case, the H_2TNPc molecules are able to slip betweeen adjacent Ag^{II}TNPc molecules and reduce the degree of inter-Ag^{II} relaxation.

Dichroic Ratio Measurements: When polarized light is used to record the electronic spectrum of a well-organized film, the absorption of the light is expected to vary with the angle between the direction of the electric vector of the light and the dipping direction when making the film. Shown in Figure 4 are the electronic absorption spectra of two Ag^{II}TNPc(-2)/SteA mixed films with the electric vector perpendicular ($E_{\perp}$) and parallel ($E_{||}$) to the dipping direction. The fact that $Abs_{\perp}$ is larger than $Abs_{||}$ suggests that most of the Ag^{II}TNPc molecules in the film tend to sit on the substrate surface with their macrocyclic plane facing the dipping direction. Moreover since this film is 12 layers thick, the films must lay down on top of one another in a well organised fashion.

A series of Ag^{II}TNPc(-2)/SteA mixtures have been investigated with the molar ratios being 2:1, 1:1, 1:2, 1:4, and 1:9, in order to determine how the SteA molecules affect the deposition of the Ag^{II}TNPc monolayer and their molecular orientation. The π-A isotherms of the five mixtures are shown in Figure 1. These illustrate that the collapse pressure of the mixed monolayer increases with the amount of SteA in the mixture; the more SteA a monolayer contains, the more difficult it will be to fold the monolayer. The experiment has also shown that when the Ag^{II}TNPc(-2)/SteA molar ratio was larger than one, the deposition ratio became less than unity, with the 2:1 mixture only exhibiting a value of 0.5. This could be understood by recalling that the pure Ag^{II}TNPc monolayer can only be transferred with difficulty.

Each film shows a dichroic effect but to a varying degree. The film with a higher Ag^{II}TNPc(-2)/SteA molar ratio gave a higher value of the dichroic ratio ($Abs_{\perp}/Abs_{||}$), indicative of a higher degree of molecular organization. Two examples are shown in Figure 4 with (a) from the 2:1 mixed film and (b) from the 1:4 mixed film, and in Figure 5 the dichroic ratios for five mixtures are plotted versus the molar fraction of Ag^{II}TNPc in the mixture. This clearly illustrates that the molecules in the mixed film become more organized with an increase in the relative concentration of

Ag^{II}TNPc. Thus the SteA molecules do not help to organize the Ag^{II}TNPc molecules but instead reduce the orderliness of the film.

Previous studies with stearic acid diluted phthalocyanine films,[23] have demonstrated the existence of aggregated domains within the stearic acid arrays. Our data suggest a similar situation. Individual aggregates show high organisation and dichroism, and at low stearic acid concentrations, neighboring domains may serve to orient each other in a parallel fashion. As the relative concentration of phthalocyanine is reduced, the domains are further apart and their orientation more random; thus the dichroism is reduced.

To gain further insight into the molecular orientation in the film, two angles, θ and ϕ, are proposed to represent the average molecular orientation. This is shown schematically in Figure 6, in which Y corresponds to the dipping direction when making the film, Z is the normal of the substrate surface and X is perpendicular to the YZ plane. If a flat circle is used to represent the phthalocyanine transition dipole plane, the angle formed by the normal (z') to the circle with respect to the Z axis will be called θ, and the angle between the projection of the normal in the XY plane and the X axis called ϕ.

Following the procedure developed by Yoneyama et al.,[31] orientation angles, θ and ϕ, for each of the five mixed films can be calculated and the results are listed in Table 1. There is no consistent change in the θ value, but the value of ϕ decreases with increasing relative concentration of SteA. Evidently the rotation of Ag^{II}TNPc molecules about their x' axis, which is parallel to the X axis, is not affected by the presence of SteA, but the rotation about the r' axis, which is perpendicular to the normal of the phthalocyanine circle and parallel to the YZ plane, will be easier if the amount of SteA is increased. Considering that a film with randomly ordered molecules should have an average ϕ value of 45° ($\int_{0^\circ}^{90^\circ}\phi d\phi/\int_{0^\circ}^{90^\circ}d\phi = 45^\circ$) and a perfectly ordered film should show 90° for ϕ, Table 1 also suggests that the molecular organization in the film becomes worse in SteA mixed films.

In summary, the above observations reveal that although the presence of SteA is necessary to obtain uniform films, the molecular organization of the film is reduced by giving more freedom of orientation for the $Ag^{II}TNPc$ molecules.

Cyclic Voltammetric Studies: An $Ag^{II}TNPc(-2)/SteA$ (1:2) mixed film (3 layers thick) was deposited onto a SnO_2 film-coated glass slide, and studied by cyclic voltammetry in a 0.2M $NaClO_4$ aqueous solution. The film voltammogram exhibited a broad and irreversible redox wave with the half-potential, $E_{1/2} = 0.65V$ (vs. SCE), as shown in Figure 7a. The redox process is a one-electron oxidation, leading to the species $[Ag^{III}TNPc(-2)]^+$ based upon the following arguments.

(1) In the solution voltammetry, $Ag^{II}TNPc$ is successively oxidized in two one-electron steps to $[Ag^{III}TNPc(-2)]^+$ and $[Ag^{III}TNPc(-1)]^{2+}$ at 0.71 and 1.19 V (vs SCE) respectively.[19]

(2) When the same kind of film, deposited on a glass slide, was oxidized chemically with chlorine gas, oxidation occurred to yield $[Ag^{III}TNPc(-2)]^+$, as indicated by electronic spectroscopy (vide infra).

(3) A spectroelectrochemical study of the film polarized at +0.75V showed a spectrum with a red shifted and slightly less intense Q-band and a new band around 440 nm (Figure 8). This is consistent with the solution spectroelectrochemical data wherein the formation of $[Ag^{III}TNPc(-2)]^+$, from $Ag^{II}TNPc$ in DCB, is associated with a red shifted and less intense Q band, and the appearance of a new absorption at 430 nm.[19] Upon re-reduction of the oxidized film by polarization at -0.05 V, the 440 nm band disappeared, and the Q band shifted back to its original position with increased intensity. This cycle can be repeated many times, but with some loss of overall Q band intensity each time, probably due to some film loss from the electrode. These observations are inconsistent with the postulate that polarization merely changes the aggregate-monomer

ratio, since such a change towards the monomer would result in an increase in intensity of the red shifted Q band.

In the solution electrochemistry, the first oxidation step of $Ag^{II}TNPc(-2)$ to $[Ag^{III}TNPc(-2)]^+$ is very broad and ill-resolved due to extensive aggregation and a kinetically slow electron transfer step. The $Ag^{II}TNPc(-2)$ LB film is also greatly aggregated, as discussed above. This molecular interaction also results in a broad CV peak for the LB film whose irreversibility is indicated by the large peak separation (E_a-E_c), of over 200mv. The differential pulse cyclic voltammogram, (in Figure 7b), shows that the peak is much smaller upon reversing the scanning. This may be associated with the movement of ClO_4^- anions through the film. Upon oxidation of the film, the ClO_4^- anions penetrate into the film to balance the positive charge. However, after their penetration, the anions are locked inside the film and have difficulty leaving on the time scale of the experiment. The scan rate dependence of the redox wave shows a nonlinear relationship between peak current and scan rate, consistent with this supposition.

Chemical Stability of the LB Film: An important property for an LB film is the stability of the molecular organization of the film against electrochemical or chemical change. We have therefore studied the change in dichroic ratio of the LB film upon electrochemical or chemical modification.

The polarized UV-Vis spectra of a $Ag^{II}TNPc(-2)$/SteA (1:2) mixed LB film (6 layers) deposited on a SnO_2-film coated glass slide is shown in Figure 9a. They resemble the spectra of the film on a regular glass slide, except for a small broad band around 500 nm, which is believed to be due to a specific interaction with the SnO_2 surface since the absorption remains if the film is oxidized or reduced electrochemically, but is not present in the solution spectrum of the film washed off the surface.

Electrochemical studies were carried out under the same conditions as those employed in the cyclic voltammetric studies. After repeating the cyclic potential scanning in the range of -0.4 to 1.0 V for 9 times, the polarized spectra were recorded (Figure 9b). The dichroic ratio when measured at the main Q-band measured close to 100 % of its original value, although the interaction absorption at 500 nm had increased. The invariance of the dichroic ratio suggests that the molecular organization within the film is stable in terms of general cyclic voltammetric measurement.

Chemical Cycling of LB Film: An $Ag^{II}TNPc(-2)/SteA$ (1:2) film (10 layers) deposited on a glass slide was treated with molecular Cl_2 gas either in the gas or aqueous phase. In the gas phase experiment, the slide was placed, for a few minutes, inside a bottle containing Cl_2 gas, approximately 0.5% by volume in air, and then removed and washed with distilled water. The resulting spectrum is shown in Figure 10b. Compared to the original film spectrum (Figure 10a), the Cl_2-treated film showed a red-shifted Q-band at 640 nm but no new band around 500 nm, consistent with the one-electron oxidation of $Ag^{II}TNPc(-2)$ to $[Ag^{III}TNPc(-2)]^+$. The Cl_2-treated film maintained the same degree of molecular organization as before, indicated by the almost unchanged dichroic ratio (1.23 in Figure 10a, and 1.19 in Figure 10b).

When the gas phase Cl_2-oxidized film was immersed in a 10% (Vol) N_2H_4 aqueous solution for 15 to 30 min., the initial Q band envelope was restored entirely with a slight decrease in dichroic ratio (to 1.17), as shown in Figure 10c. Thus the LB film can be oxidized by chlorine gas and reduced back with aqueous hydrazine without change in film organization. The spectra of the $[Ag^{III}TNPc(-2)]^+$ species in Figures 8 and 10 likely differ because the counter-ions and, possibly, coordination number are different in the two cases.

In a solution phase oxidation, the same film as above was exposed to a 0.1 M $NaClO_4$ aqueous solution bubbled with chlorine gas (10 - 20 s) for 2 minutes. In this case, the electronic spectrum again demonstrated oxidation to $[Ag^{III}TNPc(-2)]^+$ but with a slightly larger red shift in the Q band perhaps because the reaction was more complete. However the dichroic ratio was greatly reduced (Figure 11a), implying substantial loss of film organization. When this film was reduced back to Ag^{II}TNPc (Figure 11b) with hydrazine, the dichroic ratio declined almost to unity, indicating loss of order. A much thinner film (4 layers) was used to repeat the liquid phase experiment, with the same results being obtained.

Thin film reorganization upon redox sampling undoubtedly involves solvent transfer through the film.[32,33] Thus the loss of organization upon solvent phase oxidation, but retention during gas phase oxidation may reflect the disruptive effect of such solvent transport in the former case.

Summary and Conclusions: Highly ordered well behaved Ag^{II}TNPc(-2) Langmuir-Blodgett films can be co-deposited with stearic acid onto suitable substrates, with a deposition ratio of unity. Increasing stearic acid facilitates the transfer of a compact film, but decreases the degree of organization of the Ag^{II}TNPc(-2) component. The ESR spectra of the mixed Ag^{II}TNPc(-2)/SteA films show that aggregation is still occurring, evidence that the stearic acid does not interleave between the Ag^{II}TNPc(-2) molecules. Thus dilute films are likely composed of domains of aggregated Ag^{II}TNPc(-2) which are internally ordered, separated by stearic acid, but with some loss of relative organization between the domains. The presence of the dichroism in the film spectra suggests that each domain consists of Ag^{II}TNPc(-2) molecules with their macrocyclic plane tending to face the dipping direction. In the films of higher relative Ag^{II}TNPc concentration, each of the domains has a similar orientation, resulting in the anisotropic optical property. The degree of freedom with which the domains orient is dependent upon the relative amount of SteA in the mixture. A larger relative amount of SteA results in a larger degree of freedom for domain orientation and, therefore, worsens the film organization.

Film organization is largely unaffected by electrochemical cycling or by chemical cycling using gaseous chlorine and aqueous hydrazine, but the order is rapidly lost if the film is cycled using a solution chemical oxidant, perhaps due to solvent transport. Retention during electrochemical oxidation in solution shows that different solvent transport and likely anion compensation pathways occur depending upon whether the method of oxidation is chemical or electrochemical. Clearly the detailed mechanisms require further study.

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Table 1 Molecular Orientation as a Function of Molar Fraction

Mol.Frac. $Ag^{II}TNPc$	θ	ϕ
0.10	52	46
0.20	52	53
0.33	42	63
0.50	46	72
0.67	48	79

See text and Figure 6 for coordinate system.

Figure Legends

Figure 1. Surface pressure vs. area per molecule isotherms for a) pure Ag^{II}TNPc, and the five Ag^{II}TNPc(-2)/SteA mixtures with molar ratios being (Ag^{II}TNPc:SteA): b) 2:1, c) 1:1, d) 1:2, e) 1:4, f) 1:9.

Figure 2. Electronic absorption spectra of a) Ag^{II}TNPc(-2)/SteA (1:2) mixed LB film, with a thickness of 12 layers, and b) Ag^{II}TNPc(-2)/toluene solution, about 5×10^{-5}M, path length 0.2 cm, made by washing off the LB film with toluene.

Figure 3. ESR spectra of Ag^{II}TNPc(-2)/H_2TNPc(-2)/SteA (1:11:24) mixed LB film of 40 layers on quartz slide. The inset in the figure: Ag^{II}TNPc(-2)/SteA (1:2) mixed LB film of 50 layers on quartz slide.

Figure 4. Polarized electronic spectra of Ag^{II}TNPc(-2)/SteA mixed LB film (12 layers thick) with molar ratios (AgTNPc:SteA) being a) 2:1 and b) 1:4, and the electric vector of the incident light being α) perpendicular ($E_{\perp}$) and β) parallel ($E_{||}$) to the dipping direction.

Figure 5. A relationship between dichroic ratios of Ag^{II}TNPc(-2)/SteA mixed LB films and the molar fraction of Ag^{II}TNPc.

Figure 6. Coordinate system for showing the molecular orientation of Ag^{II}TNPc in the film. Y is the dipping direction, Z is the normal of the substrate surface and X is perpendicular to the YZ plane.

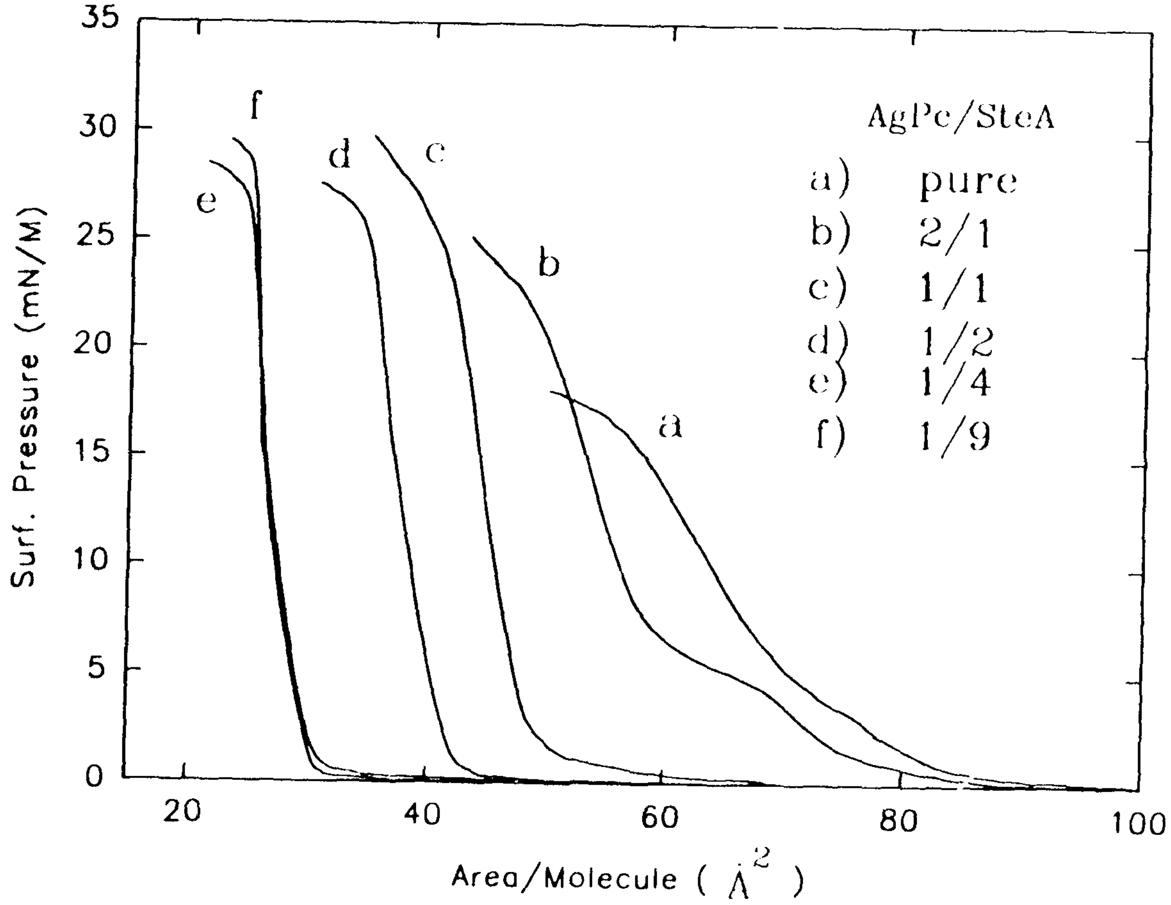
Figure 7. a) Linear cyclic voltammogram (scan rate 100 mV/s) and b) differential pulse cyclic voltammogram (scan rate 2 mV/s) of Ag^{II}TNPc(-2)/SteA (1:2) mixed LB film on a SnO_2 film-coated glass slide (8 layers thick) in 0.2M $NaClO_4$ aqueous solution.

Figure 8. Electronic spectra of Ag^{II}TNPc(-2)/SteA (1:1) mixed LB film (12 layers thick) and the oxidized species generated by potentiostatic electrolysis, the potential was set at 0.75V vs. SCE.

Figure 9. Dichroic measurements of Ag^{II}TNPc(-2)/SteA (1:2) mixed LB film (6 layers) on a SnO_2 film-coated glass slide with a) before and b) after cyclic voltammetric studies (9 cycles).

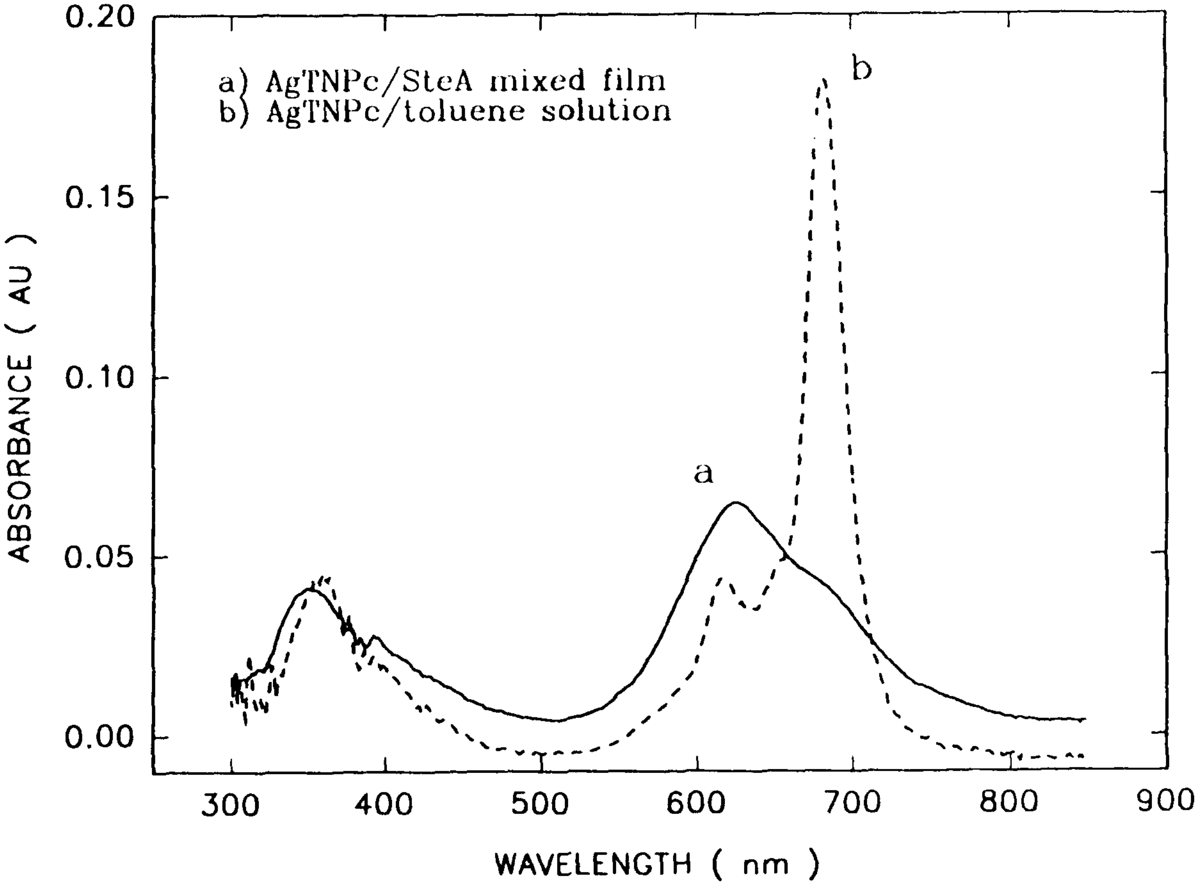
Figure 10. Polarized spectra of Ag^{II}TNPc(-2)/SteA (1:2) mixed LB film (10 layers) on glass slide upon chemical reactions: a) original film; b) 5 minute exposure to 0.5%(Vol.) Cl_2 gas in air; c) 25 minute immersion of the Cl_2-treated film in a 10%(Vol.) N_2H_4 aqueous solution.

Figure 11. Polarized spectra of Ag^{II}TNPc(-2)/SteA (1:2) mixed LB film (10 layers) on glass slide. a) The film has been treated with a Cl_2-bubbled (15 secs) 0.1M $NaClO_4$ aqueous solution for 3 minutes; b) the oxidized film was treated with a 10%(Vol.) N_2H_4 aqueous solution for 25 minutes.



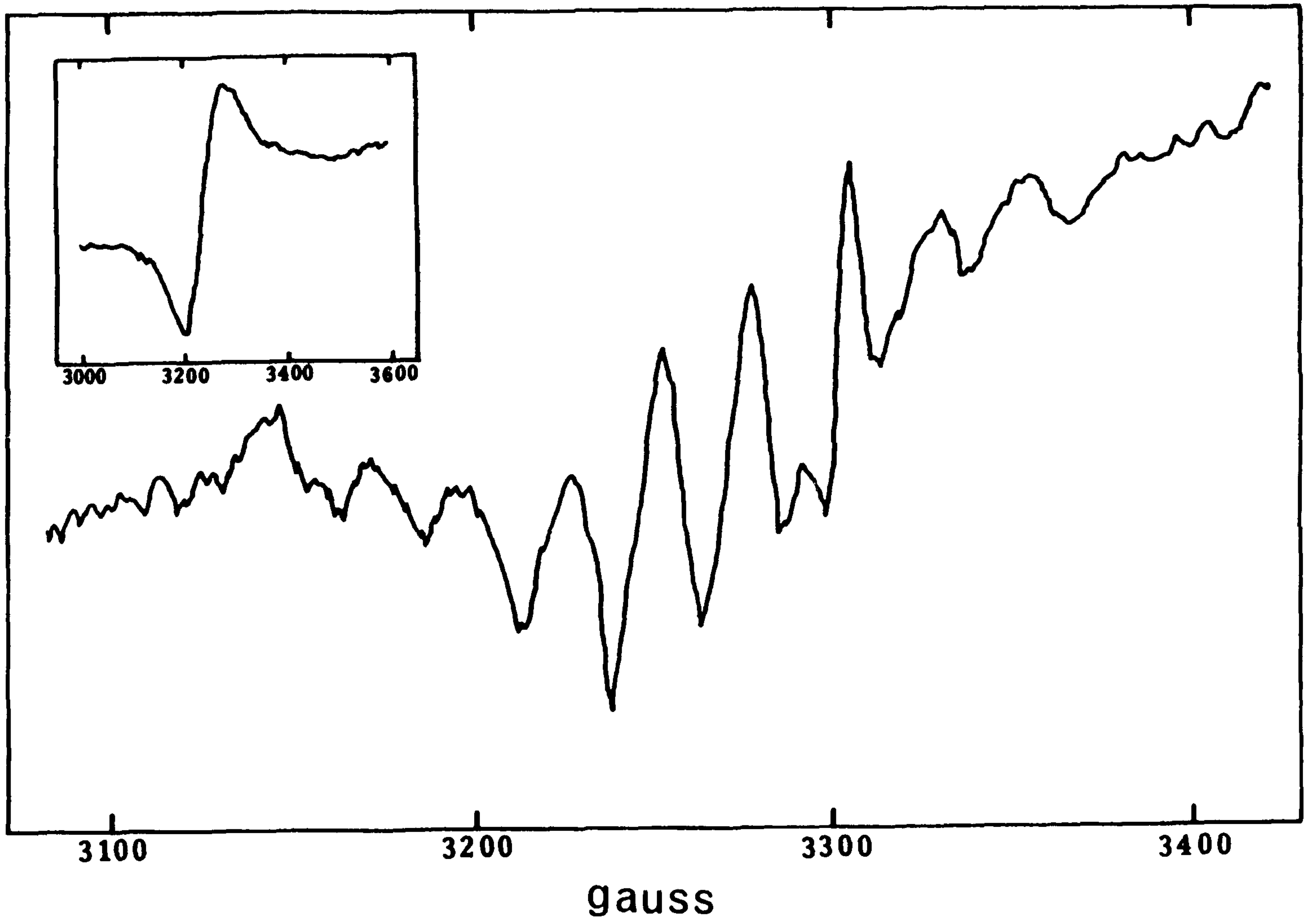
Surf. Pressure (mN/M)
35
30
25
20
15
10
5
0
20
40
60
80
100
Area/Molecule (Å^2)
AgPc/SteA
a) pure
b) 2/1
c) 1/1
d) 1/2
e) 1/4
f) 1/9
a
b
c
d
e
f

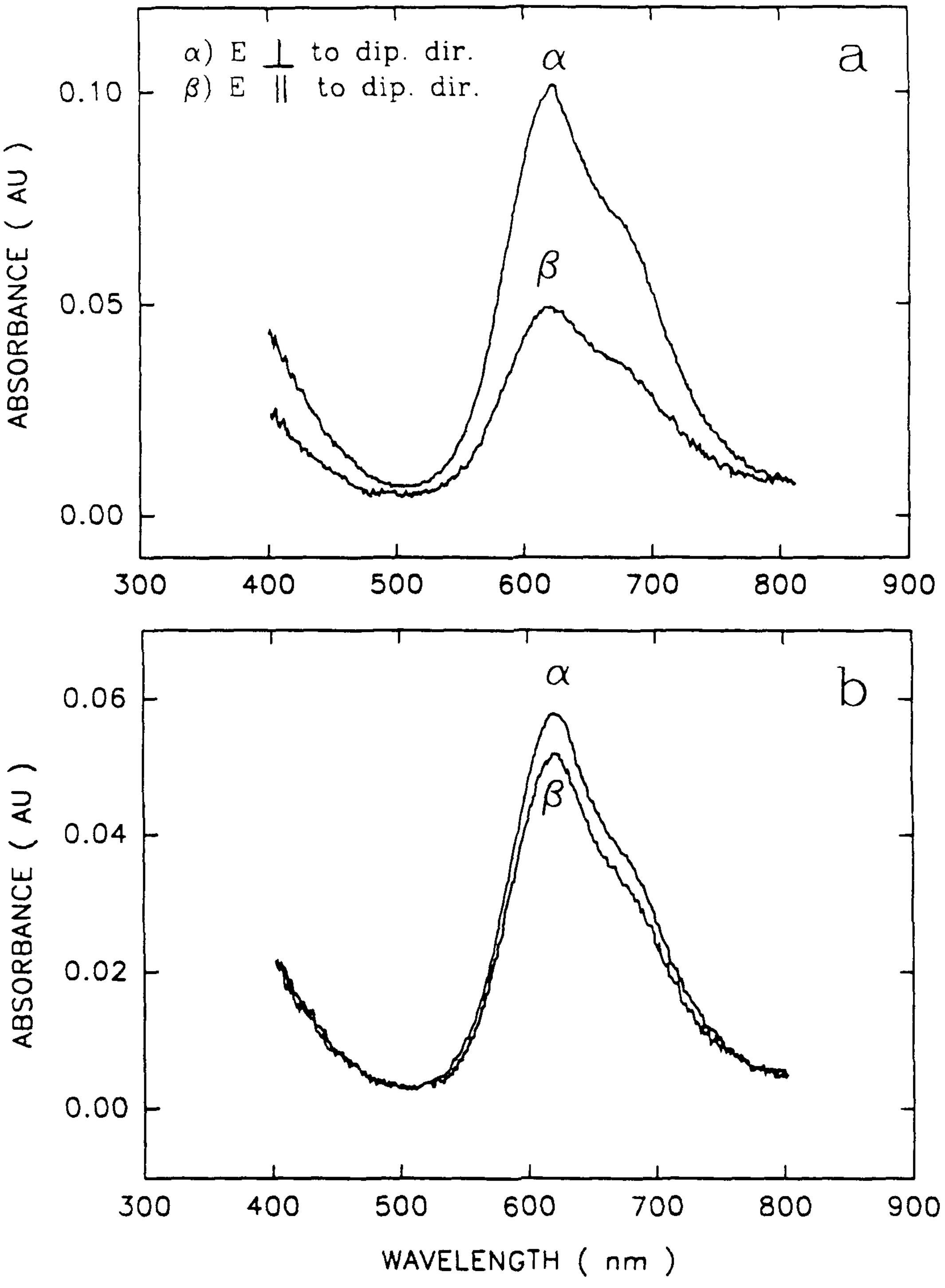
P21


a) AgTNPc/SteA mixed film
b) AgTNPc/toluene solution
a
b
0.20
0.15
0.10
0.05
0.00
ABSORBANCE (AU)
300
400
500
600
700
800
900
WAVELENGTH (nm)

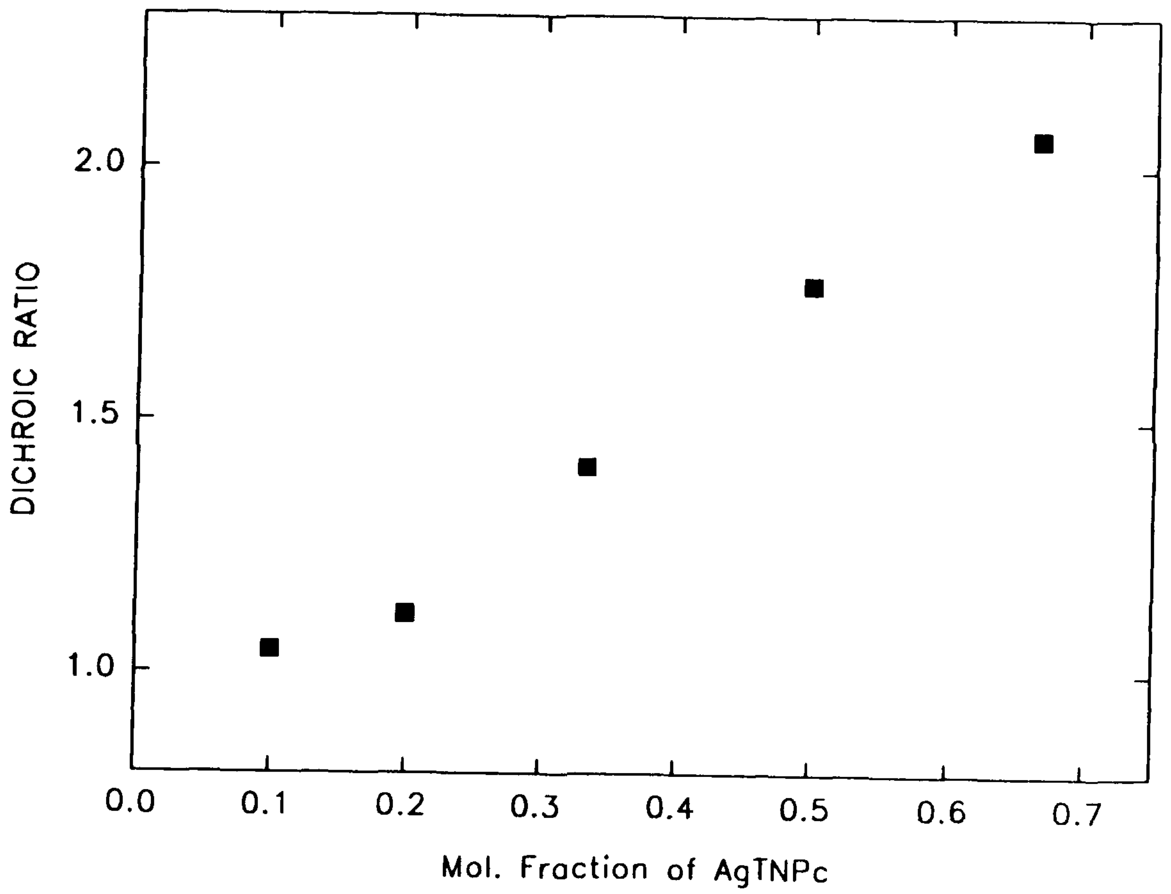
2

R22 Fig



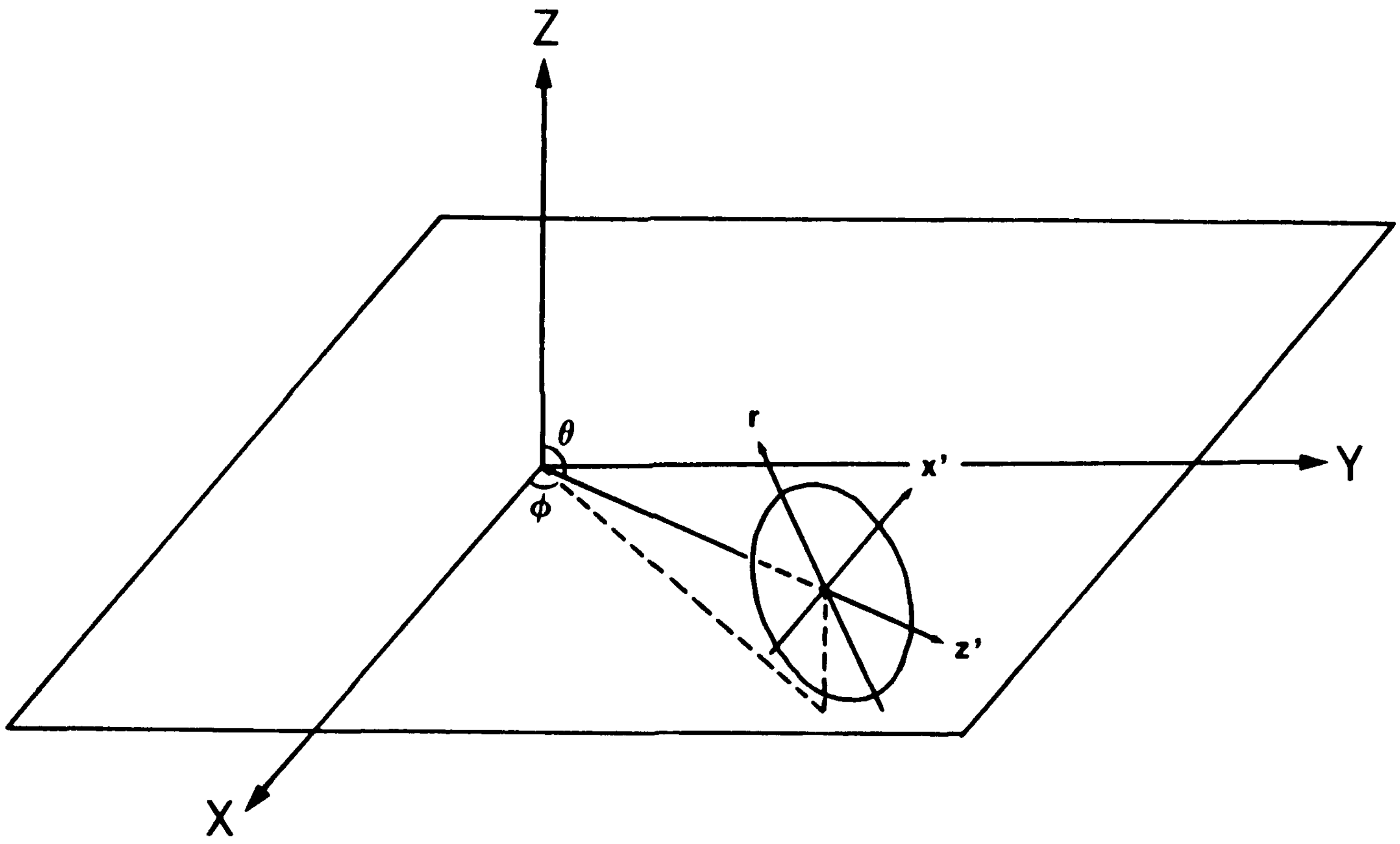


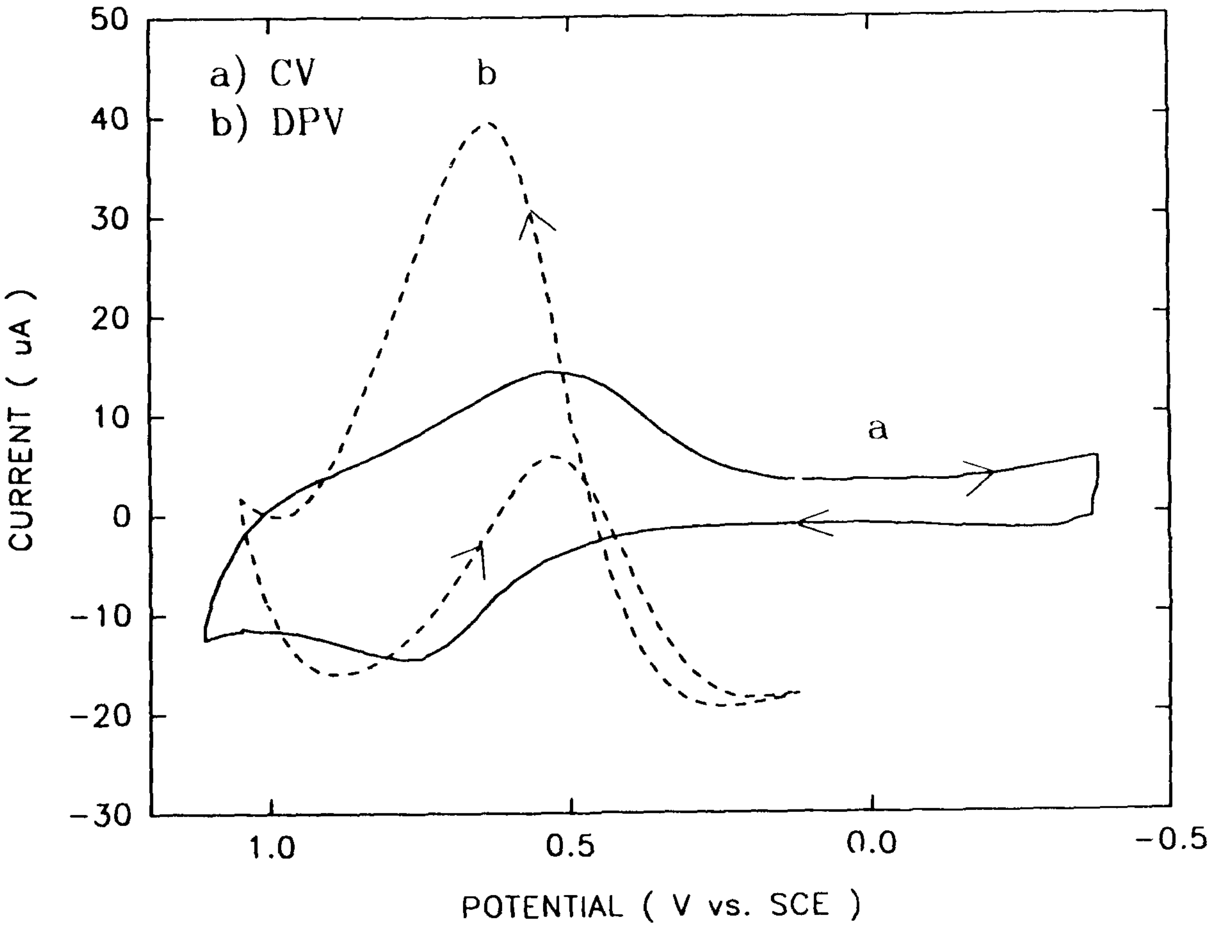
α) E ⊥ to dip. dir.
β) E ∥ to dip. dir.
α
β
a
ABSORBANCE (AU)
0.00
0.05
0.10
300
400
500
600
700
800
900
α
β
b
0.00
0.02
0.04
0.06
WAVELENGTH (nm)

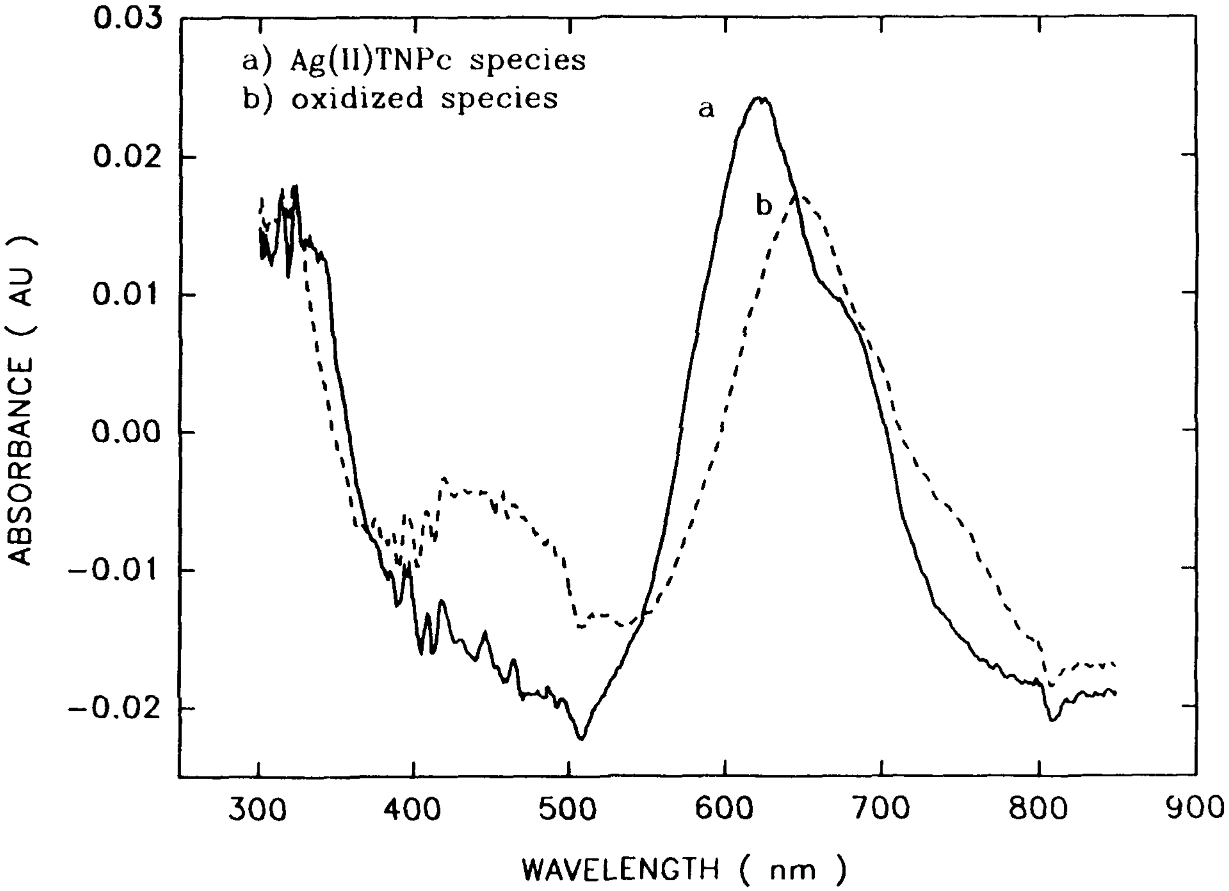

DICHROIC RATIO
1.0
1.5
2.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Mol. Fraction of AgTNPc

5

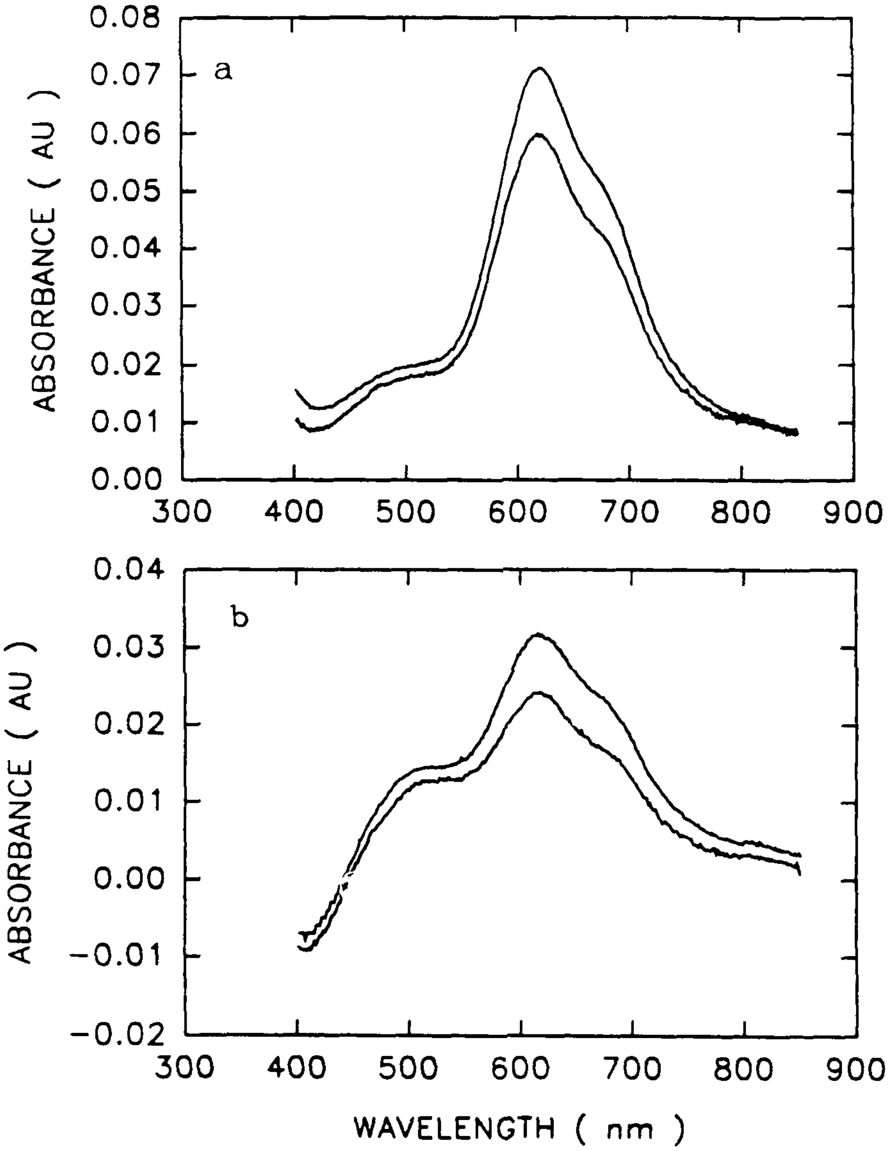
Fig.

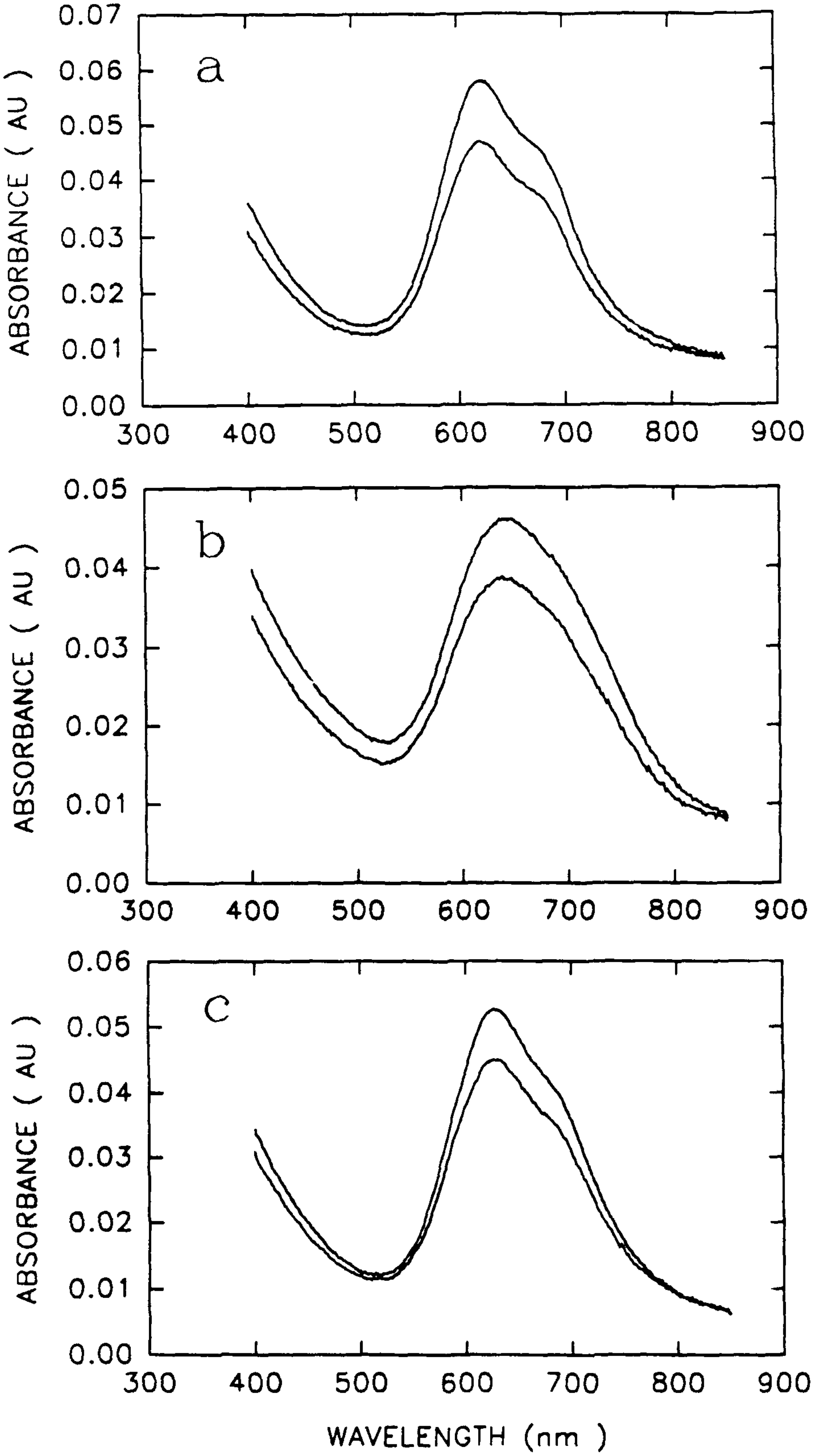


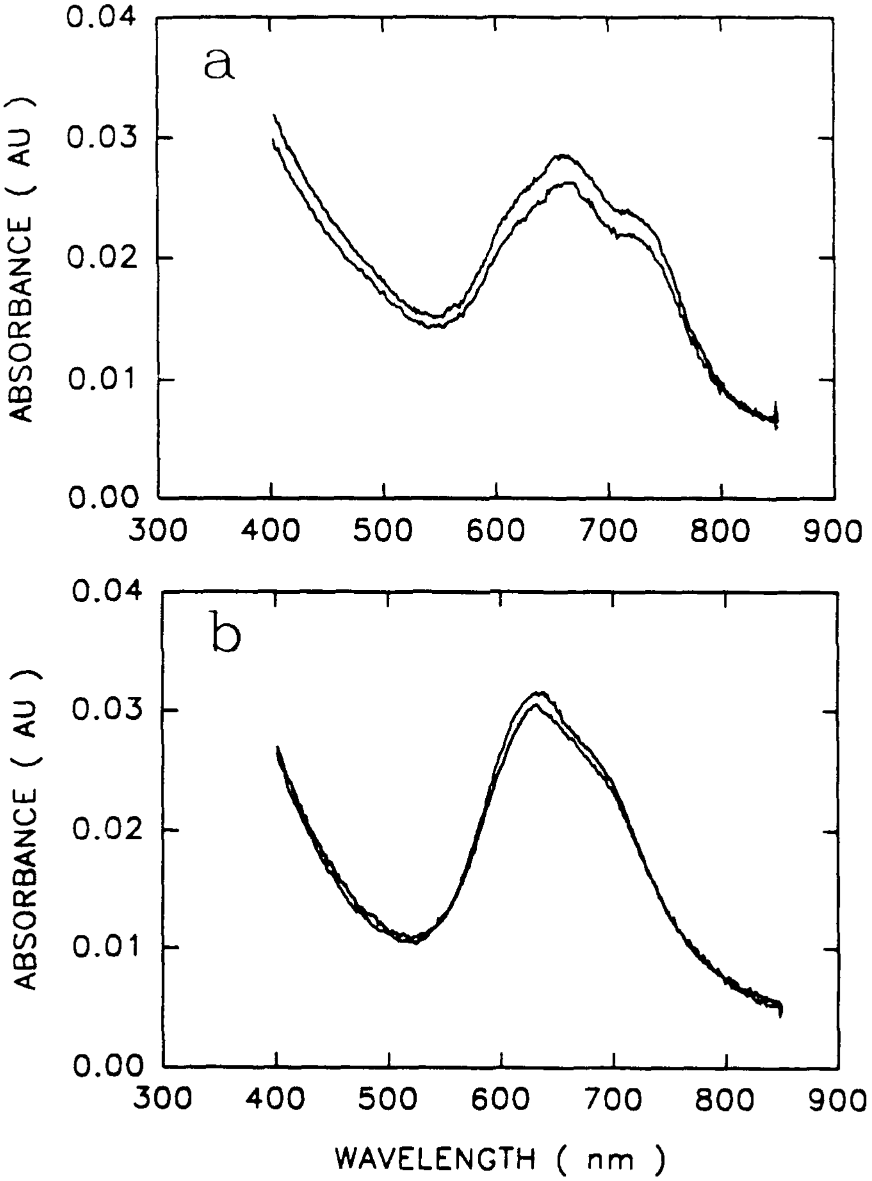

a) CV
b) DPV
a
b
CURRENT (uA)
50
40
30
20
10
0
−10
−20
−30
1.0
0.5
0.0
−0.5
POTENTIAL (V vs. SCE)


0.03
0.02
0.01
0.00
−0.01
−0.02
ABSORBANCE (AU)
300
400
500
600
700
800
900
WAVELENGTH (nm)
a) Ag(II)TNPc species
b) oxidized species
a
b

8


a
b
ABSORBANCE (AU)
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
ABSORBANCE (AU)
−0.02
−0.01
0.00
0.01
0.02
0.03
0.04
300
400
500
600
700
800
900
WAVELENGTH (nm)


a
b
c
ABSORBANCE (AU)
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
300
400
500
600
700
800
900
WAVELENGTH (nm)


a
b
ABSORBANCE (AU)
0.00
0.01
0.02
0.03
0.04
300
400
500
600
700
800
900
WAVELENGTH (nm)